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(54) **Smoke fumigant formulations.**

(57) An insecticidal and acaricidal smoke fumigant formulation is obtained by mixing granules A having a bulk specific gravity of 0.3 to 0.9 and containing a pyrethroid compound as an active ingredient, an inflammable substance and an organic blowing agent, with granules B having a bulk specific gravity of 0.5 to 1.1 and containing potassium perchlorate, potassium nitrate and/or potassium chlorate, burning agent, heat generation-regulating agent, perchlorate-decomposing aid and inorganic filler, the mixing ratio (weight ratio) of the granules A and the granules being 1 to 0.5-4.

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The present invention relates to an insecticidal and acaricidal smoke fumigant formulation, which is particularly useful for indoor uses.

For many years, mosquito coils and electric mosquito mats have widely been used to exterminate mosquitos, but they are not effective against bedbugs, house ticks (Ornithonyssus bacoti), cockroaches.

For extermination of bedbugs, house ticks, cockroaches, etc., jet-type smoke fumigant formulations have been developed.

In conventional jet-type smoke fumigant formulations, an active ingredient -- which is mixed with a smoking agent -- is jetted by the ignition of the smoking agent. The conventional jet-type smoke fumigant formulations do not exert sufficient insecticidal effects of the active ingredient because a considerable amount of the active ingredient contained in the jet-type smoke fumigant formulations is decomposed by the heat generated from the combustion of the smoking agent, and because the combustion temperature of the formulations is controlled to rather low from the standpoint of safety, and, hence, so is the vaporizing rate of the active ingredient.

Accordingly, there has been a strong demand for the development of smoke fumigant formulations, which can safely be burned to release the active ingredient at a high vaporizing rate, thereby exerting a potent insecticidal and acaricidal effects against bedbugs, house ticks, cockroaches, etc.

In order to develop much more effective and safe insecticidal and acaricidal smoke fumigant formulations, the present inventors have extensively studied, and, as a result, invented an insecticidal and acaricidal smoke fumigant formulation, which comprises: (A) 1 part by weight of granules A comprising 5 to 20 parts by weight of at least one pyrethroid compound as an active ingredient;

10 to 20 parts by weight of at least one inflammable substance selected from the group consisting of celluloid and polyvinyl nitrate; and

5 to 50 parts by weight of at least one organic blowing agent selected from the group consisting of azodicarbonamide, dinitrosopentamethylenetetramine and azobisisobutyronitrile, the bulk specific gravity of the granules A being 0.3 to 0.9, preferably 0.3 to 0.6; and (B) 0.5 to 4 parts by weight, preferably 1 to 3 parts by weight, of granules B comprising 10 to 20 parts by weight of potassium perchlorate, 3 to 8 parts by weight of potassium nitrate and/or 1 to 5 parts by weight of potassium chlorate, 7 to 20 parts by weight of at least one burning agent selected from the group consisting of starch, lactose, cellulose, sucrose, glucose, fructose and mannitol, 3 to 8 parts by weight of at least one heat generation-regulating agents selected from the group consisting of guanidine nitrate, dicyandiamide, phosphoric guanyurea and guanidine sulfamate, 15 to 30 parts by weight of at least one perchlorate-decomposing aid selected from the group consisting of potassium chloride, triiron tetroxide, sodium chloride, copper oxide, chromium oxide, iron oxide, iron chloride, active carbon and ferrocene and 20 to 50 parts by weight of at least one inorganic filler selected from the group consisting of aluminum oxide, clay, perlite, diatomaceous earth and talc, the bulk specific gravity of the granules B being 0.5 to 1.1, preferably 0.6 to 1.0.

The insecticidal and acaricidal smoke fumigant formulations of the present invention have advantages that the active ingredient is very effectively vaporized, with little decomposition, by the combustion of the formulation, and exerts a strong insecticidal and acaricidal effect against said pests, and that they can safely be used indoors since their combustion is relatively mild and the combustion temperature is relatively low.

The present invention will be illustrated below.

The pyrethroid compounds which may be used in the insecticidal and acaricidal smoke fumigant formulation of the present invention include, for example, cyphenothrin [(RS)- $\alpha$ -cyano-3-phenoxybenzyl (1R)-cis,trans-chrysanthemate], allethrin [(RS)-3-allyl-2-methyl-4-oxocyclopent-2-enyl (1RS)-cis,trans-chrysanthemate], prallethrin [(S)-2-methyl-4-oxo-3-(2-propynyl)cyclopent-2-enyl (1R)-cis,trans-chrysanthemate], tetramethrin [N-(3,4,5,6-tetrahydrophthalimido-methyl (1RS)-cis,trans-chrysanthemate], resmethrin [5-benzyl-3-furylmethyl (1RS)-cis,trans-chrysanthemate], d-phenothrin [3-phenoxybenzyl (1R)-cis,trans-chrysanthemate], permethrin [3-phenoxybenzyl (1RS)-cis,trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate], fenvalerate [(RS)- $\alpha$ -cyano-3-phenoxybenzyl (RS)-2-(4-chlorophenyl)-3-methylbutyrate], fenpropathrin [(RS)- $\alpha$ -cyano-3-phenoxybenzyl 2,2,3,3-tetramethylcyclopropanecarboxylate], trans-fluthrin (benfluthrin) [2,3,5,6-tetrafluorobenzyl (1R)-trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate], cypermethrin [(RS)- $\alpha$ -cyano-3-phenoxybenzyl (1RS)-cis,trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate], deltamethrin [(S)- $\alpha$ -cyano-3-phenoxybenzyl (1R)-cis-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate], optical isomers and stereoisomers of these compounds and mixtures thereof.

In the granules A described above, the mixing ratio of the pyrethroid compound as an active ingredient and the inflammable substance is preferably 1 to 0.8-2 (weight ratio).

The celluloid used as the inflammable substance for the granules A include the celluloid itself and solid solutions of nitrocellulose with plasticizers such as tricresyl phosphate, dibutyl phthalate and tributyl acetyl-citrate. It is preferred that the granules A contain further components, i.e. a celluloid-stabilizing agent and a heat generation-regulating agent. The amount of the former agent is 0.1 to 5 parts by weight of at least one

diphenylamine, ethyl centralit, methyl centralit and 2-nitrodiphenylamine, and the amount of the latter agent is 3 to 15 parts by weight of at least one guanidine nitrate, dicyandiamide and nitroguanidine.

If necessary, the granules A may further contain 1 to 50 parts by weight of at least one inorganic filler such as aluminum oxide, clay, talc, diatomaceous earth and perlite and 3 to 15 parts by weight of at least one blowing-regulating agents such as zinc oxide and calcium stearate. Further, the granules A may contain antioxidants (e.g. BHT), efficacy enhancer (e.g. piperonyl butoxide, MGK-264, S-421, etc.), perfumes and deodorants.

In producing the granules A, usually, the predetermined amounts of the above components and a suitable amount of water or a lower alcohol (e.g. methyl alcohol) are mixed and kneaded together, and the resulting mixture may be granulated into granules and dried according to a usual method to obtain the desired granules A. In order to facilitate granulation, it is preferred to add 0.1 to 4 parts by weight, more preferably 0.5 to 3 parts by weight of a thickening agent (e.g. methyl cellulose, hydroxypropylmethyl cellulose) as a granulation aid.

The particle size of the granules A thus obtained is usually 0.5 to 3.5 mm, preferably 1.0 to 2.5 mm.

The granules B described above may contain 0.1 to 4 parts by weight, preferably 0.5 to 3 parts by weight of a thickening agent (e.g. methyl cellulose, hydroxypropylmethyl cellulose) as a granulation aid. In producing the granules B, usually, the predetermined amount of the above components and a suitable amount of water are mixed and kneaded together, and the resulting mixture is granulated into granules and then dried the granules according to the usual method.

The particle size of the granules B thus obtained is usually 0.5 to 3.5 mm, preferably 1.0 to 2.5 mm.

The smoke fumigant formulations of the present invention are usually prepared by packing each or a mixture of the thus obtained granules A and B into a container (e.g., paper cylinder), and then setting an igniting agent such as a formed thermit.

By igniting the smoke fumigant formulation of the present invention, the vapor of the active ingredient is efficiently spread in a moment in a large space. Thus, the formulation of the present invention can effectively exterminate not only mosquitos or flies but also insanitary pests such as bedbugs, house ticks, or cockroaches hiding behind or under furnitures or other things. Moreover, from the standpoint of possibility of causing fires, the smoke fumigant formulation of the present invention is safe and, hence, particularly suited for indoor uses.

The present invention will be illustrated more specifically with reference to the following examples and comparative examples, but it is not to be interpreted as being limited to these examples.

In each example, all parts mean a part by weight.

#### Example 1

The granules A having a bulk specific gravity of 0.4 was obtained by mixing 15 parts of cyphenothrin, 17 parts of celluloid, 28 parts of azodicarbonamide, 0.4 part of diphenylamine (hereinafter referred to as DPA), 29.1 parts of perlite and 10 parts of zinc oxide, kneading and mixing the resulting mixture with 0.5 part of methyl cellulose and a suitable amount of water, granulating the resulting mixture according to a usual method, and then drying the granules.

The granules B having a bulk specific gravity of 0.92 were obtained by mixing 10 parts of potassium perchlorate, 3 parts of potassium chlorate, 10 parts of lactose, 6 parts of guanidine nitrate, 10 parts of potassium chloride, 15 parts of triiron tetroxide, 20 parts of aluminum oxide and 25 parts of kaolin clay, kneading and mixing the resulting mixture with 1 part of methyl cellulose and a suitable amount of water, granulating the resulting mixture according to the usual method, and then drying the granules.

A smoke fumigant formulation was obtained by putting 10.0 g of the granules A obtained above in a cylindrical paper container (diameter 36 mm; height 80 mm), laying a glass wool net on the granules A and then putting 15.0 g of the granules B on the net. The vaporizing rate of the active ingredient (cyphenothrin) of the resulting smoke fumigant formulation was measured according to the following method to find that it was 78%.

#### Method for measuring vaporizing rate of the active ingredient

In measuring the vaporizing rate, an instrument shown in Fig. 1 was used. One hundred grams of silica gel is packed in a glass filter 3 and the lower part of the glass filter is connected to a suction pump.

The ignited smoke fumigant formulation was immediately placed on a wire net 2a in the body 2 of a container, and the body was covered with a covering container 1. An air-drawing cock 4 is opened, and the generated smoke was suctioned at a rate of 25 ml/min. from the lower part of the glass filter.

After thirty seconds from the completion of fuming of the smoke fumigant formulation, suction was stopped. The insides of the covering container 1, the body 2 of the container and the glass filter 3 were washed with acetone, and the washings and an acetone extract obtained by extracting the silica gel in the glass filter 3 with acetone were combined. The amount of the collected active ingredient contained in the combined acet-

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Table 3  
 20 g  
 100 g

Granules A	Granules B	A:B (weight ratio)	Height of cylindrical paper container (mm)	Vaporizing rate (%)
11.3 g	9.0 g	1:0.8	50	50.1
11.3 g	11.3 g	1:1	50	53.4
11.3 g	17.0 g	1:1.5	50	66.8
11.3 g	22.6 g	1:2.0	50	64.5
11.3 g	28.3 g	1:2.5	70	58.5
11.3 g	33.9 g	1:3.0	70	54.1
11.3 g	39.6 g	1:3.5	70	51.7

8.4  
 7.5  
 6  
 5  
 4.3  
 3.8  
 3.3

15g → 100g A  
 17g = x  
 17 → 20.3  
 x = 11.3

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An example of an insecticidal test using the smoke fumigant formulation of the present invention will be shown below.

## Example 7

In a large chamber which is a rectangular parallelepiped having a floor area of 300 cm x 400 cm and a height of 230 cm were put two plastic cups 10 which contained 10 German cockroaches (*Blattella germanica*) and two plastic cups 11 which contained 5 American cockroaches (*Periplaneta americana*) as shown in Fig. 2. Separately, a corrugated cardboard box 12 of 30 cm x 30 cm x 30 cm was prepared, and a slit of 5 mm x 10 cm was made at each central part of four sides of the box so that it was parallel to the floor. The box was then set on the floor of the chamber. Further, one plastic cup containing 10 German cockroaches and one plastic cup containing 5 American cockroaches were also put in this corrugated cardboard box. The smoke fumigant formulation obtained in Example 1 was ignited and put on the center 13 of the floor of the chamber, and the inside of the large chamber was smoke fumigated. After 3 hours, the cockroaches were taken out of each plastic cup and transferred to a clean container containing bait and water. After 3 days, the condition, dead or alive, of the cockroaches were observed.

As a result, it was found that the mortality of the test cockroaches was 100%.

That is, the cockroaches could be effectively controlled because the generated smoke fumigant entered the corrugated cardboard box even through the slits made in the box.

## BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a sectional view of the instrument used to measure the vaporizing rate of the smoke fumigant formulations of the present invention in Examples 1 to 6 and Comparative Examples 1 and 2.

Fig. 2 is an illustrative view of the large chamber used to confirm the cockroach-controlling effect in Example 7.

1. Covering container
2. Body of the container
- 2a. Wire net
3. Glass filter
4. Air-drawing cock
10. Plastic cup containing German cockroaches
11. Plastic cup containing American cockroaches
12. Corrugated cardboard box
13. Position at which the smoke fumigant formulation was set.

## Claims

1. An insecticidal and acaricidal smoke fumigant formulation comprising granules A having a bulk specific gravity of 0.3 to 0.9 and granules B having a bulk specific gravity of 0.5 to 1.1, said granules A comprising 5 to 20 parts by weight of at least one pyrethroid compound as an active ingredient, 10 to 20 parts by weight of at least one inflammable substance selected from the group consisting of celluloid and polyvinyl nitrate and 5 to 50 parts by weight of at least one organic blowing agent selected from the group consisting of azodicarbonamide, dinitrosopentamethylenetetramine and azobisisobutyronitrile, said granules B comprising 10 to 20 parts by weight of potassium perchlorate, 3 to 8 parts by weight of potassium nitrate and/or 1 to 5 parts by weight of potassium chlorate, 7 to 20 parts by weight of at least one burning agent selected from the group consisting of starch, lactose, cellulose, sucrose, glucose, fructose and mannitol, 3 to 8 parts by weight of at least one heat generation-regulating agent selected from the group consisting of guanidine nitrate, dicyandiamide, phosphoric guanyurea and guanidine sulfamate, 15 to 30 parts by weight of at least one perchlorate-decomposing aid selected from the group consisting of potassium chloride, triiron tetroxide, sodium chloride, copper oxide, chromium oxide, iron oxide, iron chloride, active carbon and ferrocene and 20 to 50 parts by weight of at least one inorganic filler selected from the group consisting of aluminum oxide, clay, perlite, diatomaceous earth and talc, and the mixing ratio (weight ratio) of said granules A and granules B being 1 to 0.5-4.  $\frac{1}{0.5} - \frac{4}{1}$  2-4.
2. A formulation according to Claim 1, wherein the granules A contain 0.1 to 5 parts by weight of at least one celluloid stabilizing agent selected from diphenylamine, ethyl centralit, methyl centralit and 2-nitrodiphenylamine, 3 to 15 parts by weight of at least one heat generation-regulating agent selected from guanidine nitrate, dicyandiamide and nitroguanidine, and 0.1 to 4 parts by weight of at least one granulation aid selected from methyl cellulose and hydroxypropylmethyl cellulose, and the granules B contain 0.1 to

4 parts by weight of at least one granulation aid selected from methyl cellulose and hydroxypropylmethyl cellulose.

3. A formulation according to Claim 1 or 2 wherein the bulk specific gravity of the granules A is 0.3 to 0.6.
- 5 4. A formulation according to any one of the preceding claims, wherein the bulk specific gravity of the granules B is 0.6 to 1.0.
- 10 5. A formulation according to any one of the preceding claims, wherein the mixing ratio (weight ratio) of the granules A and the granules B is 1 to 1-3.
6. A formulation according to any one of the preceding claims, wherein the mixing ratio (weight ratio) of the pyrethroid compound and the inflammable substance in the granules A is 1 to 1-2.
- 15 7. A formulation according to any one of the preceding claims, wherein the pyrethroid compound is cyphe-  
nothrin, allethrin, prallethrin, tetramethrin, resmethrin or d-phenothrin.
8. A formulation according to any one of the preceding claims wherein the pyrethroid compound is cyphe-  
nothrin or d-phenothrin.
- 20 9. A method for controlling insects and acarines which comprises fumigating a locus where insets and/or  
acarines inhabit with a formulation as claimed in any one of Claims 1 to 8.
10. Use of a formulation according to any one of claims 1 to 8 as an insecticide or an acaricide.

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FIG. 1

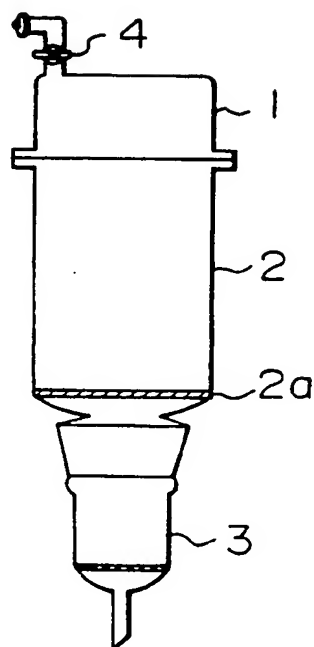
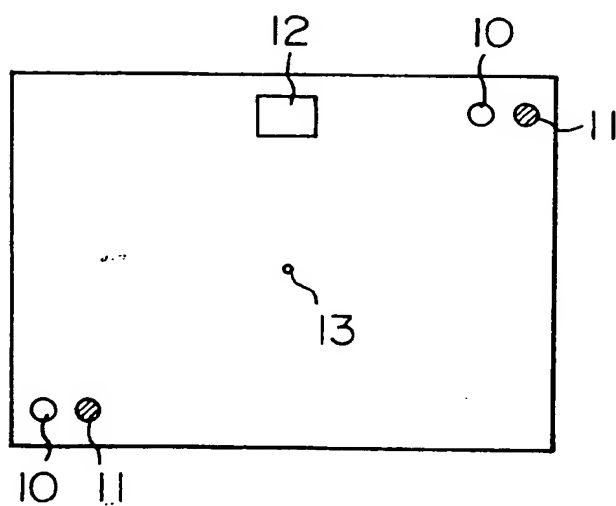


FIG. 2





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54 **Smoke fumigant formulations.**

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European Patent  
Office

# EUROPEAN SEARCH REPORT

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EP 94 30 6062

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	PATENT ABSTRACTS OF JAPAN vol. 016, no. 244 (C-0947) 4 June 1992 & JP-A-04 054 102 (NAMIKATA JIYOCHIYUUFUN SEIZOUSHIYO:KK) 21 February 1992 * abstract *	1-10	A01N53/00 A01N25/18
Y	PATENT ABSTRACTS OF JAPAN vol. 007, no. 252 (C-194) 9 November 1983 & JP-A-58 140 002 (TAISHO SEIYAKU KK;OTHERS: 01) 19 August 1983 * abstract *	1-10	
Y	DATABASE WPI Section Ch, Week 7951, Derwent Publications Ltd., London, GB; Class C03, AN 79-91914B & JP-A-54 145 217 (MATSUMOTO M) 13 November 1979 * abstract *	1-10	
Y	US-A-4 228 124 (EARTH CHEMICAL COMPANY) 14 October 1980 * the whole document *	1-10	TECHNICAL FIELDS SEARCHED (Int.Cl.6) A01N
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 13 March 1995	Examiner Klaver, J
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			

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